NOTES ON KARL FISCHER REAGENT

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A review of the literature discloses that many formulas have been proposed for the preparation of the Karl Fischer reagent. Because of the great dissimilarity of the amounts of the ingredients proposed by the different investigators (1, 2, 3, 4, 6, 7), it is impossible to make a direct comparison of the formulas. A possible cause of this diversity may have been the example of Karl Fischer (3), who expressed the ingredients of his reagent in grams, although he used gram molecular weights. Had he stressed the gram molar ratios which he actually used, these diverse formulas might have been avoided.

Typical of these formulas are the two following preparations of the reagent: (a) Weigh into a flask 3.785 liters (1 gallon) of 2-A pyridine and

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add 203 grams of liquid sulfur dioxide for each kilogram of pyridine. To 1359 grams of stock-pyridine-sulfur dioxide solution in a 5-liter container add 1786 grams of alcohol, mix and cool to room temperature. Add 453.6 grams (1 pound) of iodine, stopper, cool under running water before shaking, then alternately swirl and cool until the iodine is in solution (1); and (b) 502 grams anhydrous pyridine, 102.5 grams of sulfur dioxide, anhydrous; 202 grams of iodine, reagent quality; 1000 ml anhydrous methanol (4). It is not apparent that these two reagents have identical molar ratios of sulfur dioxide, iodine and pyridine, since the weights specified appear to have no relation to their gram molecular weights. Actually, if the weights of these substances in the two solutions are expressed as gram moles, with the moles of iodine taken as unity, the ratios become 1:2:8 for iodine, sulfur dioxide and pyridine, and the two solutions are identical except for the methanol used, which is 1420 and 1206 ml respectively per mole of iodine.

Table 1 gives the formulas of the six preparations of the reagent often

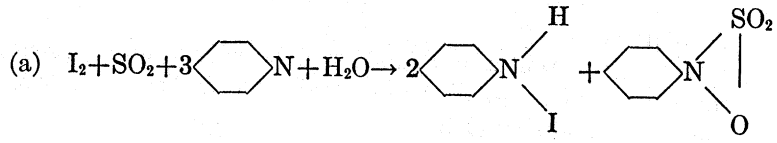
TABLE 1.—*Karl Fischer Reagent*

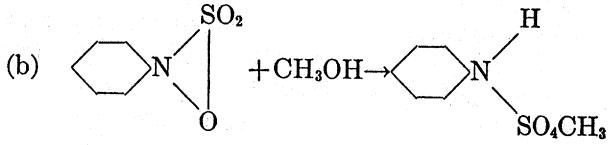
AUTHOR	FORMULAS FOR PREPARATION				MOLAR RATIOS			VOLUME PER MOLE OF IODINE
	IODINE	SULFUR DIOXIDE	PYRIDINE	METHANOL	IODINE	SULFUR DIOXIDE	PYRIDINE	METHANOL
	g	*g*						*ml*
Almy (1)		753	3.785 l		1	2	8	1420
	453.6 ←To 1359 g add→ 1786 g							
ERRL	238	183	752	427 ml	1	3	10	400
Fischer (2)	254	192	790 g	5000 ml	1	3	10	5000
Johnson (3)	169	128	425 ml	511 ml	1	3	8	767
Journal Amer. Oil Chem. Soc. (4)	202	102.5	502 g	1000 ml	1	2	8	1206
Smith (6)	84.7	64	269 ml	667 ml	1	3	10	2000
Wernimont (7)	500	380	1700 ml	200 ml	1	3	10	102

referred to, together with their calculated molar ratios. The table not only aids in the selection of an appropriate reagent but also serves as a guide in comparison of results obtained by the different reagents. It is easily seen that all the molar ratios show marked similarity and that the reagents differ only in concentration, which is dependent on the amount of methanol used per mole of iodine.

The methanol is not expressed on a gram molar basis because only a portion of it is used as a reactant; the remainder serves principally as a solvent and diluent. Mitchell (5) and Smith (6) have suggested that the methanol combines in a 1:1 molar ratio (eq. b), with the inner salt of the

pyridinium hydroxide-N-sulfonic acid formed in the reaction of the Karl Fischer reagent with water. One mole of the complex is formed from one mole of iodine according to reaction (a). Thus an equivalent of 1 mole of methanol is required for each mole of iodine.





Besides the 1 gram mole required in this reaction, additional methanol must be present to serve as a solvent for the products formed. However, a large excess of methanol, such as that used by Fischer (2), is to be avoided, for it sets up conditions conducive to side reactions with aldehydes and ketones, forming acetals and ketals (6). These side reactions result in high and erroneous water values. By reducing the methanol and increasing the pyridine, Smith obtained a reagent that reacted normally in the presence of aldehydes and ketones.

In titrating large amounts of water a reduction in the volumes of reagent is made possible by using a more concentrated reagent. A satisfactory reagent for 40 to 400 mg of water has 400 ml of methanol per mole of iodine. To use less than 400 ml per mole of iodine gives a reagent with such a high concentration that errors in measuring may occur when ordinary laboratory volumetric apparatus is used. A reagent with the molar ratios 1:3:10 for iodine, sulfur dioxide, and pyridine and with 400 ml of methanol will have a titer of approximately 7.8 mg of water per ml of reagent.

Of the two methods commonly used for titrations with Karl Fischer reagent—the visual and electrometric end points—the electrometric method is most applicable for general and intermittent use. Here identification of the end point is not limited to analysis of colorless or light-colored solutions, but can be used equally well with dark-colored materials. The electrometric end point is easy to detect and usually provides a warning as the end point is approached. The visual method, although limited to colorless or light-colored solutions, is well suited to routine analyses.

STANDARDIZATION

Karl Fischer reagent is standardized with a known weight of water, either added directly or contained in a methanol solution; the reaction

end point is detected visually or electrometrically. Standardizing the reagent by the visual end point method is relatively simple because it consists in only two steps (a) measuring the volume of the reagent consumed by a given volume of methanol, and (b) measuring the volume of the reagent consumed by an equal volume of methanol containing a known weight of water (5, 6). The water titer of the reagent (standardization) is obtained from the two volumes of the reagent. Since the visual method of standardization is not applicable to such strong reagents as recommended here because of the uncertain color of the end point, the electrometric method should be used. This method overcomes the problem of end-point color, but to obtain maximum sensitivity the procedure of titration should be reversed (1, 7), that is, titrate the reagent with the water-methanol solution. As used in the past, standardization of the reagent by this method was objectionable because it required (a) anhydrous methanol, (b) weighed small portions of water (8), or (c) of hydrated substances as primary standards (5).

The authors suggest an alternative method. This method avoids use of anhydrous methanol, small weighed portions of water, or hydrates of uncertain composition. The standard water-methanol solution is made by adding 4 grams of water, weighed to the nearest 0.1 mg. with a weight burette, to 200 ml of reagent-grade methanol. This solution is then made up to 2 liters with more of the methanol. It is desirable that the methanol contain less than 0.2 per cent water, a condition met by most reagent-grade methanols, so that excessive amounts of the Karl Fischer reagent will not be consumed. The water content of the prepared standard water-methanol solution is the sum of the water present as impurity, plus that added. In the proposed method, the titer of the Karl Fischer reagent is easily obtained by using only three titration steps (a, b, and c) and then substituting the volume values in a simple equation. Only the weight of the added water in the standard water-methanol solution need be known.

PROCEDURE

(a) A few milliliters, usually 5, of Karl Fischer reagent are added to the reaction vessel to provide anhydrous conditions. The excess reagent is destroyed by addition of the standard water-methanol solution.

(b) A second portion, 10–25 ml of Karl Fischer reagent, accurately measured to the nearest 0.01 ml, is added and titrated with the standard water-methanol solution. From the volume of standard water-methanol solution and the volume of Karl Fischer reagent, the ratio of standard water-methanol solution to reagent is found.

(c) A quantity of the reagent methanol and a known volume of Karl Fischer reagent, in excess of the water in the added reagent methanol, are added. The excess of Karl Fischer reagent is then back-titrated with

standard water-methanol solution. The titer of the reagent can be calculated by means of the following equation.

$$\frac{WQM}{Q + P - MR} = \text{mg of } H_2O/1 \text{ ml Karl Fischer reagent}$$

$$M = \frac{\text{volume water-methanol solution}}{\text{volume of Karl Fischer reagent}} \quad \text{(step b)}$$

W = weight of added water in mg per ml of the water-methanol solution
Q = volume of reagent methanol (step c)
R = volume of Karl Fischer reagent (step c)
P = volume of standard water-methanol solution (step c)

The analysis of a sample is performed in much the same manner.

The system is freed of water as done in step (a) of the above standardization procedure. Then (step d) an amount of the Fischer reagent is added which is known to be in excess of that required by the sample. The sample is now added and the mixture stirred, preferably by a magnetically driven "flea," and the amount of Fischer reagent that is in excess to that required by the water of the sample is determined by back titration with the standard water-methanol solution.

$$\%\text{ water in sample} = \frac{(\text{ml KF reagent added} - \text{ml. KF reagent} \simeq \text{std water-methanol}) \times \text{water titer of KF reagent} \times 100}{\text{wt. sample}}$$

This method provides a simple and convenient means of standardizing the Karl Fischer reagent, avoids the preparation of absolutely anhydrous methanol and the difficulties inherent in the weighing of small amounts (100 to 200 mg) of water using ordinary laboratory apparatus.

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